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NEW DEVELOPMENTS IN COTTON -- AN OLD CHEMURGIC CROP [1,2]

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A revolutionary idea of science, probably largely the result of research events during the last war, seems to be replacing the old concept of science as a field limited in interest only to a few. The down-to-earthness, as well as the tremendous importance of science, has been pressed in upon the layman, and has revealed the scientist to him as a man of practical objectives. These new concepts are favorable for implementing the aim of chemurgy, namely, the development of additional uses for farm crops through applied chemistry. Progress in agricultural science has naturally been speeded by this renewed interest in chemurgy.

Actually, of course, the application of chemistry for the greater industrial utilization of farm commodities was practiced, although not so consciously, long before the term chemurgy was invented. Recently, however, there has been a keener awareness of the effectiveness of this means of guiding surplus agricultural crops into specific fields of usefulness so as to obtain maximum national economy. There has been also a wider recognition of the need for concerted action and leadership if these revolutionary developments are to be fully utilized. In a sense my own organization, the Southern Regional Research Laboratory of the U. S. Department of Agriculture, has been established in response to this call for action and leadership.

Because of the broad scope of the subject of chemurgy, I have narrowed my evaluation of present-day achievements to those of the cotton crop. The maintenance of cotton as a leading crop, admittedly essential to the economic national welfare, may well require in the future the discovery of new uses as well as improvement in its present uses. Cotton, indeed, is a logical raw material for further adaptation to nonfood uses. Before the relatively recent development of crushing cottonseed for edible oil, it was the most important soil-grown crop consumed entirely in nonfood uses. Besides its vast use in apparel and household articles, cotton is consumed in an almost limitless number of strictly industrial items. In addition, the chemical structure of cotton -- and of this I shall speak again later -- is ideal for the application of treatments for the formation of new cellulose compounds with a wide range of usefulness.

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[1] Report of a study in which certain phases were carried on under the Research and Marketing Act of 1946.

[2] Address before the Southwest Regional Meeting, American Chemical Society, Shreveport, Louisiana, December 10, 1948.

[3] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Many undeniable improvements have been brought about lately in cotton and cottonseed products, through the accumulation of research facts, which point clearly to several new uses. None of these, it is true, has yet reached the proportions of some of the older achievements of cotton. Cotton's world-wide rise to textile supremacy by the end of the eighteenth century; the spectacular discovery almost within our own time of the rich potentialities of cottonseed; and even the challenge over the last 20 years to cotton's world lead in textiles and domestic lead in oilseeds, are instances of the drama that has traditionally attended developments in connection with this unique farm commodity. But, while not in the least spectacular, recent research findings, when considered in relation to the present defensive position of cotton -- still the supreme fiber, but threatened by competition from rayon and other synthetic fibers -- make us aware of the full possibilities of the research approach to the improved usefulness of cotton. This, I believe, will be apparent in the examples of current cotton and cottonseed activities at the Southern Regional Research Laboratory which I am going to describe to you.

Our ultimate goal in research at the regional research laboratories is the maintenance, enlargement, or creation of uses for agricultural products, as a means of providing farmers larger and more stable markets and of offering industry new outlets for capital. Obviously, we keep constantly in mind that research developments to be of value for industry must be applicable economically on a large scale. We do not forget that many of our studies may apparently progress only slowly, requiring years before results are visible in terms of dollars and cents. We are aware continually that a far greater basic knowledge of the chemical and physical properties of many of the crops we study is needed to enable us to realize our ideal of service. We know also that eventual profits of research to agriculture and industry will depend upon the success with which these two groups are able to evaluate developments in relation to consumer demands. Finally, we remember that extensive cooperative work between scientists, farmers, and industrialists is essential for the full accomplishments of our mutual objectives. In our work on cotton and cottonseed at the Southern Regional Research Laboratory we have had many instances of the advantages to be gained through such collaboration.

COTTON LINT

In chemical research on cotton lint we follow three principal lines of investigations: We search continually for new knowledge of the fundamental chemical constitution and behavior of cotton cellulose; we seek the formulation of chemical finishes which will enhance the natural fine qualities of cotton materials or improve them in qualities in which they are less well established; and we attempt the chemical modification of cellulose to create entirely new characteristics. While we also pursue intensively research on mechanical processing of cotton and have developed several new and improved machines which give more efficient and economical manufacture of high-quality cotton yarns and fabric, I shall devote my discussion today to the chemical types of investigation mentioned as I believe these will be of greater interest to this audience.

Fundamental Investigations

At the Southern Laboratory we attach a great deal of value to fundamental studies as an essential part of utilization research. They quite often supply the data upon which important commercial developments are based. Some of the new knowledge we have acquired has contributed significantly to the field of cotton chemistry. I shall take time to describe briefly only a few of these studies:

Information has been acquired regarding the shape of the basic structural unit of cellulose which is of a broad enough nature to provide a basis for studying the shape of the molecules of other carbohydrates in solution. There is a relation between the structure of the carbohydrate molecule and the shift in the optical rotation of the new structural units formed when cellulose is dispersed in cuprammonium solution. These findings should lead to increased knowledge of the nature of the chemical and biological reactions of carbohydrates. A method developed for determining the methoxyl group in methanolyzed cellulose has aided in this research.

The rate of hydrolysis, or the conversion of cellulose to sugars, has also been a useful technique in investigating the structure of cotton fiber. The different rates of hydrolysis observed provide a means of distinguishing between the amorphous and crystalline cellulose in the fiber. The ratio of amorphous to crystalline cellulose is related to many of the useful properties of the fiber -- for example, the degree of its impermeability to water.

Other interesting new techniques, besides the two I have mentioned, have been developed at the Southern Laboratory to aid in fundamental investigations. The determination of the fluidity of cellulose in solution is used as a measure of degradation. Up to now a cuprammonium solution has been commonly used for fluidity determinations. Recently, chemists at the Southern Regional Laboratory have developed an improved technique using cupriethylamine diamine hydroxide solutions as a solvent for cellulose in viscosity measurements. In the improved technique the better features of other cupriethylamine diamine hydroxide solutions have been incorporated. Advantages are that the cupriethylene diamine reagent is less volatile than cuprammonium and does not need to be refrigerated during preparation and use. In addition the cellulose solutions prepared with it are more stable to the oxidizing influence of the air than those prepared with cuprammonium reagent. With the technique it is possible to apply a convenient method of adjusting for velocity gradient which we had previously worked out for cuprammonium solutions of cellulose. An outline of the technique has been adopted as a tentative standard by The American Society of Testing Materials.

Improving Cotton in Resistance to Rot and Weather

The speaker who follows me on this program will discuss the urgent need of cotton fiber improvement if competition from rival materials is to be successfully met. I need only remind you that while cotton fiber remains superior in many textile properties, there are several important respects in which competitive fibers are getting ahead, and in which, therefore, it is imperative to improve cotton. For example, improvement in cotton's rot- and weather-resisting properties would help to retain or expand many of its outdoor uses. Cotton fabrics serve under many conditions where they are under the constant attack of rot-producing micro-organisms or are in continual exposure to the sun and other degrading elements of weather. The prolonged life of cotton in such service is of interest to both agriculture and industry, and the work at the Southern Regional Research Laboratory has been carried out in cooperation with these groups.

Rotproofing by partial acetylation. A rot-resistant cotton has been produced through the chemical modification of cellulose to form a rotproof compound, unchanged in physical appearance. This is also accomplished without damaging the other important textile properties of cotton. (Most other known rotproofing treatments produce objectionable color, odor, toxicity, or other harmful effects.)

Following the development of this process in England for other purposes, we initiated a research program to utilize partial acetylation as a possible method of improving the rot resistance of military-type cotton sand bags. Our tests of the treated bags piled in stacks on the ground in New Orleans were the first to demonstrate the superior resistance to rot of partially acetylated cotton when in contact with destructive micro-organisms in the soil. The selection of partial acetylation as a method was not by pure chance, but rather by the evaluation of experimental results which indicated that micro-organisms attack cellulose at the hydroxyl groups. It followed that little or no attack would take place if the hydroxyl groups were suitably blocked. Our research showed this to be true. We have found that very excellent rot resistance is obtained when only one-third to one-half of the available hydroxyl groups are blocked.

The process, applied to fiber, yarn, or cloth, involves the controlled esterification of hydroxyl groups of the cellulose in cotton. The reaction is similar to any esterification reaction using an acid anhydride, a catalyst, and a solvent. Acetic anhydride is used as the acid anhydride, perchloric acid as the catalyst, and glacial acetic acid as the solvent. Since it is not necessary to esterify all the hydroxyl groups, time of reaction, concentration of chemicals, and temperature are controlled so that a suitable degree of acetylation takes place.

In current work an exact determination is being sought of the degree of acetylation needed in specific rot-resistant products. In addition, the principles involved in the application are being reinvestigated, with the idea of discovering a production method that would be entirely feasible for large-scale commercial use. Simplification and speeding up of the process are being attempted, through use of continuous processes to replace batch methods.

Acetylated yarns and fabrics are produced on a semicommercial scale at the Southern Laboratory to obtain samples for interested industrial companies to try out in actual service. Many industries and individuals have tested and are testing partially acetylated cotton for such varied uses as fish nets, shoe linings, and water-softening bags. In all cases where destruction was caused by rotting or mildewing our product showed excellent resistance. The results of tests on water-softening bags will illustrate the improvement. Cotton bags used in home water-softening units have a useful service life of only 1 month. Partially acetylated cotton bags have been in service for as long as a year without loss in tensile strength or sign of attack. As a result of these tests, partially acetylated water-softenting bags are being produced on a small commercial scale and the manufacturer is making plans to increase his rate of production.

While rot resistance is the property of acetylated cotton of the greatest interest to farmers, the acetylated material, as with any other new fiber, has acquired other improved chemical and physical characteristics. Some of these are electrical resistance, of interest to the varnished or cambric tape industry; greater dimensional stability with variations in relative humidity, of interest to the laminated plastics industry; and better resistance to heat degradation, of interest to laundries, using mangles and presses where the paddings and cover cloths are subjected to elevated temperature.

Weatherproofing. The most significant result of research on weatherproofing at the Southern Laboratory is the extensive amount of new fundamental knowledge which we have accumulated on the complex mechanism by which cellulose breaks down and the variable nature of the degradation suffered. These data were collected over a period of 5 years in tests of representative cotton fabrics exposed outside throughout the year on racks in the moist climate of New Orleans. Both untreated and chemically treated fabrics were evaluated. The treatments included fungicides, water-repellents, and ultraviolet-screening pigments. Interpretation of the data showed that in dry places sunlight is the principal cause of damage; but that in moist, warm climates, the attack of mildew or other micro-organisms may be a greater cause of failure. As a result of this work valuable patterns of weathering degradation were established for different types of fabrics. These are proving useful in current research on the formulation of protective finishes.

In one series of studies, a means was found for isolating the effect of sunlight from the other degrading elements of weather. A special cabinet was constructed which excludes wind, rain, dust, and micro-organisms, and is controlled automatically to rotate slowly but continuously so as to keep facing rays of the sun at normal incidence throughout the day. Fabric samples are placed behind six glass windows, five having each a different color, thus transmitting a different fraction of sunlight, and the sixth transmitting total sunlight. Data which were collected on the radiant energy incident upon each sample and on the chemical and physical evidences of deterioration showed that the ultraviolet rays are more damaging than others, but that rays of certain wave lengths may interact in such a manner as to reduce the net degrading effect of their combined incident energy. Similar data have been obtained with the use of a carbon arc lamp as a source of radiation and Corning glass filters as a means of obtaining certain selected spectral regions of incident energy.

In present weatherproofing research, we are concentrating upon prolonging the service life of two classes of cotton goods in wide use outdoors and in which good resistance to sunlight is essential; namely, the heavy ducks used in tent and awning fabrics, and the light-weight, open-weave fabrics used to shade acreages of tobacco plants.

Heavy cotton duck samples, treated with urea-formaldehyde resin alone and also in combination with mineral pigments, have been exposed in New Orleans and three other locations. At the end of a year, ducks treated with urea-formaldehyde resin in combination with lead chromate showed less than 5 percent loss of strength, compared to a loss of about 50 percent in untreated fabrics.

Because of these results with cotton duck, a similar treatment was tried in work on cotton shade cloth. A simple pigment treatment appears the most feasible -- lead chromate precipitated into the cloth has given the best results so far. This pigment was applied in a Florida plant on laundry-type equipment to 10,000 yards of cloth put into service in Florida tobacco fields in the 1948 season. After the season's use, the treated cloth had lost only 25 percent of its strength in contrast to 70 percent by untreated cloth. More extensive tests are being planned for the 1949 season.

Water-Resistant Cotton

Improvement in the water resistance of cotton fabrics will be a major need if cotton continues to be faced with its present competitive position. Therefore, this property is receiving attention at the Southern Regional Laboratory.

Impermeability to the passage of water is being sought largely through the production of swelling-type, or self-sealing-type, water-resistant fabrics. A search is being made for the cotton varieties more suitable than others for utilization of self-sealing by swelling -- that is, those having the greatest capacity upon wetting to close up the space between fibers and thus render the yarns, or the cloth, more resistant to penetration by water. In early work, the discovery was made that not only might differences be expected from variety to variety but that the immature fibers of a variety differed from the mature fibers of the same variety. This difference was discovered by means of a method applied in a specially designed apparatus. This method provides a measure of the quantity of water which under constant pressure will seep through a weighed bundle of yarn or of loose fiber, tightly packed into an orifice. By use of this orifice test it was demonstrated that seepage of water through bundles of equal weights of fibers from any variety of cotton was from 3 to 7 times greater for the mature or thick-walled fibers than for immature or thin-walled fibers. Microscopical measurements of the changes in dimensions of cross sections of individual fibers, swollen with water, indicate that fiber shape and size may greatly outweigh the influence attributable to differences in the absolute swelling values of different cottons.

We have made application of these findings in fabrics woven from yarns indicated by orifice tests as having a good degree of impermeability, and subsequently treated with a water-repellent agent; or, before weaving, we have added highly swellable finishing agents to the yarns, such as hydroxyethyl cellulose. In preliminary tests of fabrics of identical construction, those woven from yarns containing immature fibers have shown distinctly superior water resistance as compared to fabrics from mature fibers. The indicated superiority of immature fibers in this property may lead to significant developments in connection with the utilization of immature cottons.

Chemically Modified Cotton

I said awhile ago that cotton fiber is an ideal material for the application of chemurgy -- that is, for the formation of new products through chemical changes in composition. Cotton is almost all cellulose, a carbohydrate containing reactive hydroxyl groups that readily combine with acids and alcohols to form esters and ethers. This conversion to cellulose derivatives gives the treated cotton new and useful characteristics. This, therefore, is one avenue by which we seek cotton improvement at the Southern Laboratory. As a result of research in this line, we have recently produced several entirely new types of fabrics, and have effected the conversion without the loss of fibrous qualities or any significant changes in strength or appearance.

A new method of replacing a hydroxyl group with an amino ethyl group by treatment with amino ethyl sulfuric acid has been developed. The resulting cotton fabric has acquired new and interesting properties, such as the ability to take wool dyes readily and to act as an anion exchanger. A second type of cotton fabric improved in a specific quality is one having a very much more speeded-up rate of water absorption than that of ordinary cotton. This is accomplished by partial carboxymethylation of the cellulose. Besides the more rapid rate of absorption, the total amount of water taken up is also increased. The carboxymethyl groups are introduced by treating yarn or cloth with alkali and small amounts of chloracetic acid.

The phosphorylation of cotton cellulose, originally accomplished as part of a wartime project which successfully produced flameproofed cotton, has been carried out by treatment with urea and phosphoric acid followed by heating. The results indicate the presence of a mono-substituted ester. There is no evidence of the formation of other more highly substituted products, predicated in certain commercial processes by their inventors. The phosphate groups in cellulose phosphates may be replaced by halogen to give a stable product. Cellulose phosphate has also been prepared by using phosphorous oxychloride in the presence of pyridine. We have demonstrated that phosphorylated cotton is a good cation exchanger in experiments on the preparation of protein of low-mineral content.

A fourth kind of modified cellulose molecule is obtained by treating cotton with anhydrous hydrochloric acid dissolved in methanol. The short-chain cellulose molecule so produced differs from the original compound in that it has become an alkali-stable, non-reducing substance.

COTTONSEED

Cottonseed research at the Southern Regional Laboratory has yielded many interesting new facts of both scientific and practical value.

Cottonseed was little more than a waste material before the Civil War; but by 1870 crushing of the seed was established as an industry based upon the value of the oil for making soap, foods, shortening, and other products. By the end of the nineteenth century, cottonseed was the foremost oil-producing seed in the United States and held this position until surpassed by soybeans in 1944. Yet many of the values of cottonseed are not being fully exploited. Unless more of these potentialities can be realized, cottonseed may lose further ground to other oilseeds.

Improved methods of processing cottonseed for oil and meal are badly needed. While overall improvements have been made in factory operations through the years, the present methods of extracting the oil and meal with hydraulic or screw-type presses are almost the same as those used 20 years ago. Recently, at the Southern Laboratory research efforts have been directed towards making changes of a radical type, both in the usual mechanical methods and in the development of the newer solvent-extraction method.

With present hydraulic and screw pressing, there are two disadvantages: Precooking of the seed at high temperatures is practised, which damages the protein; and the method leaves an appreciable percentage of oil in the meal. Elimination or reduction in the severity of the precooking would result in an improved meal containing protein suitable for industrial uses and the recovery of the wasted oil would increase the oil production annually by over 100 million pounds. If, further, a way could be found to remove certain toxic elements which mechanical methods leave in the cooked cottonseed, the meal would be suitable for additional uses as a feed. Although the hydraulic- and screw-pressed meals, as generally obtained at present, are extensively used for feeding cattle and sheep, they contain unidentified substances which make them unsuitable for feeding some other species of livestock, particularly swine and poultry.

In contrast to the mechanical methods of extraction, the solvent-extraction method removes almost all of the oil from the meal, and the lower temperatures used leave the protein undamaged. At the Southern Laboratory we have been a pioneer group in the experimental solvent extraction of cottonseed. Only recently has this method of extraction been applied to cottonseed on a commercial scale in the United States. Several plants using solvent extraction equipment and processing have been constructed, and these are now in full operation or in experimental production.

All of the methods of processing have been complicated by problems arising from the presence of pigments in cottonseed. The speaker who preceded me on this program has acquainted you with the nature and occurrence of cottonseed pigments. This unique system of pigments, constituting about 1 to 2 percent of the entire seed, is responsible for objectionable color in the oil and meal and affects the food and feed value of the meal.

New Solvent Method of Fractioning Cottonseed

In view of this situation, a revolutionary solvent method of preparing cottonseed which we have recently developed on a pre-pilot scale at the Southern Laboratory is creating wide interest throughout the cottonseed industry. We had earlier made the important discovery that the pigments occur in glands in the seed. In attempting to separate these glands from the surrounding tissues, our chemists developed a solvent method which separates the kernel into three distinct fractions: intact, or unruptured, pigment glands; an oil-solvent mixture; and an almost oil-and pigment-free meal. The recovered oil is relatively light-colored and is of a high-grade commercial quality. The meal obtained by this unique method of processing is essentially free of pigment glands, which distinguishes it from that obtained by the usual methods. Pigment glands, which comprise 3 to 4 percent of the meats, are also recovered.

Evaluation of Deglanded Meal and Pigment Glands

Deglanded meal and pigment glands have been produced in sizeable quantities and samples have been sent out to various industrial, university, State, and Federal laboratories for evaluation of quality. Cooperating laboratories that have completed feeding experiments with deglanded meal report that it is superior in nutritive value to ordinary cottonseed meal as a source of vegetable protein in the diet of poultry. In one laboratory, feeding experiments carried out for 4 weeks, starting with 2-week-old chicks, showed superior growth with deglanded meal as the sole source of protein, without addition of an animal-growth factor to the diet. The hatchability of eggs laid by hens fed deglanded meal as the sole source of protein and without addition of the animal-growth factor was also superior. These results are particularly significant to the poultry industry, because the growth factor for chicks has previously been found only in fish solubles, high-grade meat scraps, and other feeds that have been in short supply. This cooperative research is being continued to obtain further confirmation of the results already reported and to extend the feeding experiments to other farm animals.

Preliminary investigations of the composition and properties of the separated pigment glands, undertaken in collaboration with other agencies, indicate the possibility of developing important pharmaceutical uses for them.

The process-development research has not only made available quantities of pigment glands and deglanded meal for utilization studies, but has provided valuable engineering data. Industry is cooperating with the Southern Regional Laboratory in further development of the process for commercial application.

Other Processing Research

In another line of work, designed to improve the mechanical methods of extracting cottonseed, experiments were conducted to obtain a better understanding of the influence on final product quality of the method of preparing the meats prior to expressing the oil. Seeds were cooked in the laboratory at various temperatures, with and without added moisture, and the oils obtained were analyzed for refining and bleaching performance. It was found that by cooking the seed in the presence of relatively large amounts of added moisture, oils of prime quality could be obtained. Preliminary tests in cooperation with a commercial mill show that with the screw-press method the meats should be cooked at a low temperature without added moisture to obtain oil of low initial bleach color and low rate of increase in color during storage, as well as a meal of definitely improved nutritional value.

Method for Determining Gossypol Content

Another accomplishment in our research on cottonseed pigments is the development of an improved analytical method for readily determining gossypol in both the seed and in the oil and meal. With this method it will be possible to evaluate the effect of various methods of processing on the gossypol content of the extracted products.

Cottonseed Storage

Moist cottonseed undergoes decomposition during storage, which represents a great hazard to individual oil millers, and also causes serious monetary losses annually to the industry as a whole. Therefore, chemists at the Southern Laboratory have sought to develop a better method of reducing this spoilage than that offered by the present aeration methods. Finding that certain chemicals were very successful in preventing changes in the seed during storage, they developed a treatment which consists of applying small quantities of a special chemical to the seeds while they are being conveyed to the storage bins. This method is effective alone and even more so when used in addition to forced-draft cooling. All together 50 chemicals have been found successful in inhibiting deterioration. The interest of oilseed processors in applying the treatment has been demonstrated by their cooperation in carrying out storage experiments on a semi-commercial scale at several mills in widely different locations.

CONCLUSION

I might discuss so many other phases of our research on cotton and cottonseed that I must choose a stopping place arbitrarily. The range of the problems facing cotton is, indeed, so great that even the numerous investigations followed in our work are but representative of the avenues by which cotton improvement might be approached. Fortunately, a large number of research institutions besides our own, and also countless industrial groups, are engaged in exploring cotton's possibilities. We believe that research can meet and is meeting many of the needs of cotton in its present challenged position. We are also certain that only through continued extensive research can entire hopefulness for the future of cotton be warranted.